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HYGROGEN GAS GENERATION RESEARCH AND THE RESOLUTION OF PROGRAMMATIC ISSUES IN THE DOE COMPLEX

Prepared for:

National Transportation Program
U.S. Department of Energy
Albuquerque, New Mexico

Prepared by:

J. G. McFadden
Waste Management Federal Services, Inc., Northwest Operations
Richland, Washington

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CONTENTS

LIST OF ABBREVIATIONS

ANSI	American National Standards Institute
CFR	Code of Federal Regulations
CH	contact-handled
CoC	Certificate of Compliance
D&D	decontamination and decommissioning
DEB	1,4-bis(phenylethynyl)benzene
DOE	Department of Energy
DOT	Department of Transportation
EM	Environmental Management
IE	Inspection and Enforcement
IGA	interstitial gas analysis method
INEEL	Idaho National Engineering and Environmental Laboratory
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
LOI	Loss on Ignition
MDP	Matrix Depletion Program
MIS	Materials Identification and Surveillance
NM	neutron moderation method
NRC	Nuclear Regulatory Commission
PFP	Plutonium Finishing Plant
PNNL	Pacific Northwest National Laboratory
PVC	Polyvinylchloride
RFETS	Rocky Flats Environmental Technology Site
SARP	Safety Analysis Report for Packaging
SFE	supercritical CO_2 fluid extraction method
SRS	Savannah River Site
SS&C	Sand, slag, and crucible
TRU	transuranic
TRUCON	TRUPACT-II Content Codes
VOCs	volatile organic carbons
WIPP	Waste Isolation Pilot Plant

HYDROGEN GAS GENERATION RESEARCH AND THE RESOLUTION OF PROGRAMMATIC ISSUES IN THE DOE COMPLEX

1.0 INTRODUCTION

Hydrogen gas generation issues have been an area of concern for the transport and storage of radioactive materials in the Department of Energy (DOE) Complex for a number of years. The mechanism of radiolytic formation of hydrogen gas is the interaction of radioactive decay with hydrogenous materials such as water, plastics, and oils. Radioactive wastes, residues, and nuclear materials frequently contain hydrogenous matter that generates hydrogen. The potential for a detonation or deflagration of flammable gases in a package containing radioactive materials is mitigated by not allowing a flammable mixture.

Hydrogen gas generation issues are made more complex by the wide variety of wastes, residues, and nuclear materials that exist within the DOE Complex. For instance, the Rocky Flats Environmental Technology Site (RFETS) alone has plutonium metal, plutonium oxides, plutonium fluorides, sand slag and crucible, and approximately 106 MT bulk of decontamination and decommissioning (D&D) low level waste which include solid inorganic and organic materials of different types. Because the hydrogen gas generation rate is not only dependent upon the hydrogenous matrix that is present, but also upon the isotope, decay type, age of the material, and configuration, hydrogen gas generation solutions will be case specific with no single generic answer suitable for all situations.

This report identifies some of the major hydrogen gas generation programmatic issues within the DOE Complex and the research that has been and is being conducted to address hydrogen gas generation concerns. Section 2 discusses regulatory requirements and the affect they have had on shippers. Section 3 discusses hydrogen gas generation issues that exist at some of the DOE sites and the research that is being conducted to mitigate the concerns. Section 4 provides a summary of issues and corresponding experimental research. It also identifies areas in which further research is needed.

2.0 REGULATORY REQUIREMENTS

Regulatory requirements have slowly been reflecting the growing concern surrounding the potential for hydrogen gas generation in packages containing nuclear materials and wastes. In part, the growth of hydrogen gas generation issues and concerns is due to the fact that the scope of work within the DOE complex has changed. As sites change from production mode to environmental remediation and facility closure, a wider variety of materials is being shipped for testing, processing, or final storage than has been shipped in the past. In the Nuclear Regulatory

Commission (NRC) arena, the clean up effort at Three Mile Island was among the first instances when hydrogen gas generation in the transportation of Class 7 (radioactive) materials was noted as a potential problem. Likewise, in the DOE community, the mixture of Class 7 and hydrogenous materials found in the clean up of wastes and the shipment of residues resulting from plutonium processing has increased the potential for hydrogen gas generation.

The lack of well defined criteria that addresses calculational and testing methodology has caused problems. For instance, the following questions have not been conclusively resolved: is inerting acceptable for prevention of a flammable gas mixture, when can only analytical methods be used to determine if a flammable mixture is present and when is testing required, what analytical model(s) is(are) acceptable, what are acceptable G values, can getters or recombiners be used, is deflagration/detonation acceptable provided the package is robust enough to maintain containment after a potential event, and others. In the face of this seeming lack of direction, Safety Analysis Report for Packaging (SARP) applicants have been hesitant to provide more information than needed. It is only recently that applicants have begun to accept that flammable gas analysis/testing must be approached with the same rigor as, say, structural or thermal analyses. Within the packaging community, there has existed a reluctance to accept that a SARP must demonstrate through testing or analysis, or both if necessary, that a package will contain less than 5% hydrogen gas generation by volume in half the expected shipping time (or one year). There is a trend towards clarifying regulations and standards. Lawrence Livermore National Laboratory (LLNL) has been commissioned by the NRC to write a hydrogen gas NUREG. In addition, an American National Standards Institute (ANSI) Standard committee on gas generation in packages is in the formative stages. Hopefully many of the hydrogen gas generation issues will be answered in the near future. The following sections discuss regulatory history, the movement towards more clearly defined criteria, and some of the issues that exist that are due to lack of clarity.

2.1 NUCLEAR REGULATORY COMMISSION (NRC)

Inspection and Enforcement (IE) Information Notice No. 84-72: *Clarification of Conditions for Waste Shipments Subject to Hydrogen Gas Generation* (NRC 1984) is a memo published by the NRC Office of Inspection and Enforcement in 1984. It established basic guidelines for hydrogen gas generation. The memo required that in twice the expected shipping time hydrogen gas be limited to a molar quantity that is no more than 5% by volume of the secondary container gas void at STP. Failing that, the secondary container can be inerted to ensure that oxygen is limited to 5% by volume in the portions of the package that could have hydrogen greater than 5%. The IE Information Notice provided general guidance for the preparation of SARPs until the publication of NUREG 1609.

NUREG-1609, *Standard Review Plan for Transportation Packages for Radioactive Material (Draft)*, (NRC 1997) has superceded NRC (1984) for Type B packages. It requires that an applicant for a Certificate of Compliance (CoC) for a package demonstrate in a SARP that hydrogen and other flammable gases comprise less than 5% by volume of the total gas inventory within any confined volume. It also requires that the maximum normal operating pressure within the vessel be appropriately evaluated.

In addition, NRC shipments must meet Department of Transportation (DOT) requirements. The DOT requirement in 49 *Code of Federal Regulations* 177.848 “Segregation Table for Hazardous Materials” does not allow flammable gases and radioactive materials to be loaded, transported, or stored together in the same transport vehicle or storage facility unless separated in a manner that would allow no commingling.

2.2 DEPARTMENT OF ENERGY (DOE)

Within the DOE Complex, no criteria addressing hydrogen gas generation issues in transportation packages has been defined. DOE Implementation Guide for DOE Order 460.1A (DOE, 1997) *Implementation Guide for Use with DOE O 460.1A Packaging and Transportation Safety*, requires that a SARP be sufficiently detailed to determine “. . . that the package is designed and analyzed in sufficient detail and should document the adequacy of the packaging with respect to 10 CFR 71 standards or the equivalency thereto. These regulations state that a package must meet containment, radiation control, and subcriticality assurance requirements when subjected to specified normal transport and hypothetical accident conditions.” The Implementation Guide also states that additional guidance for SARP preparation can be found in other NRC Regulatory Guides.

Guidance for long-term storage of plutonium metals and oxides is contained in DOE-STD-3013-96 (3013 standard) (DOE 1996). The 3013 standard applies to storage of packaged plutonium metals, alloys, and oxides. The standard requires that oxides be calcined and exhibit less than a 0.5 mass percent loss-on-ignition (LOI) after heating at 1,000 °C (1,832 °F) or higher for at least one hour. Metals must be inspected to ensure that no liquids are present. The materials are doubly encapsulated in metal cans that contain a maximum of 4.4 kg material. The standard conservatively assumes that all of the hydrogen in the water adsorbed in oxides is radiolytically freed to generate hydrogen gas. It contains a pressure equation used to calculate the resulting pressure from hydrogen and helium (resulting from alpha decay).

A new standard entitled, *Stabilization, Storage, and Packaging of Plutonium-Bearing Materials* (DOE 1999) is being drafted to replace the 3013 standard. The new standard will more than double the material that may be packaged for storage as it reduces the mass of plutonium required and includes uranium. The new standard allows materials with greater than 30 mass-percent uranium or plutonium where as the 3013 standard applied to material with greater than 50 mass-percent plutonium. It also incorporates engineered materials such as reactor fuel and sintered uranium/plutonium oxide pellets. In addition, the new standard allows measurement of residual water by approved techniques other than LOI. An important point made in the new standard is that pure and impure oxides contain an oxygen sink, so no flammable mixture of gases is present. The old and new standards apply to storage of materials. In preparing safety documentation for certification of new or ammended SARPs, applicants for certifications have erroneously assumed that if materials meet the 3013 standard they will be approved for shipment under a SARP. However, this is not the case. DOE package certification reviewers have requested that applicants prove by testing or analysis that a flammable gas mixture does not exist in the void volume of the inner-most confinement layer.

EM-70 has the approval authority for DOE Certificates of Compliance (CoCs). CoCs have become more restrictive in the wording regarding hydrogen gas generation. The CoC for the 9965 package signed February 26, 1999, states that: "Hydrogen gas generation in the contents shall be limited to no more than five volume percent hydrogen in any confined volume within the package. This limit applies for one year from closure of the package; shipment must be completed within this time."

2.3 NEW REGULATORY GUIDANCE

As previously stated, the NRC has commissioned LLNL to write a NUREG on hydrogen gas generation. The NUREG is due to be published in December 1999 and, although a draft has been completed, it is not currently available to the general public. The NUREG will provide criteria for hydrogen gas limits within packages. It will outline a general model for use in calculating hydrogen gas generation in packages. It also will provide information on G values for compounds and waste categories. The NUREG does not address the generation of hydrogen from water adsorbed in nuclear materials, nor does it discuss inerting, getters, or matrix depletion.

In addition to the NUREG, an ANSI Standard Committee on flammable gas generation is being formed. The Standard, ANSI N14.32, is entitled, *Gas Generation in Packages Used for Storage or Transport of Radioactive Materials.* The purpose of the ANSI standard is to provide a systematic approach for determining if a radioactive material package contains a flammable mixture of gasses and to provide a consistent approach for evaluating pressure buildup in a package due to gas generation. The NUREG and the ANSI standard will provide guidance and information that will clarify hydrogen gas generation issues.

3.0 HYDROGEN GAS GENERATION ISSUES AND RESEARCH

The following sections summarize the hydrogen gas generation issues at various sites within the DOE Complex. It is recognized that the following is not a complete list of the problems that may exist, but it is an attempt to identify some of the hydrogen gas generation issues and discuss the research that is being conducted to mitigate concerns. Note: research results are a moving target. A great deal is being done to mitigate hydrogen gas generation and, as research progresses, the areas of concern will change.

3.1 ROCKY FLATS

The programmatic driver at RFETS is the deinventory of the site for closure of Rocky Flats. The accelerated closure schedule of 2006 calls for special nuclear material to be gone from Rocky Flats by the end of 2002.

Following is a listing of the inventories that may be directly affected by hydrogen gas generation concerns. (Thorp 1999) The disposition of the inventory discusses current plans and lists issues that may still need to be addressed.

INVENTORY	*DISPOSITION*
Pu oxides	The oxides will be calcined and packed in 3013 standard cans to go to the Savannah River Site (SRS) and Los Alamos National Laboratory (LANL). LANL has tested RFETS' oxides in the Materials Identification and Surveillance (MIS) Program to determine if a higher moisture content can be allowed in a container. In addition, SRS is addressing the shipment of oxides in the 9975 container, a DOE-certified package. A white paper has been written by SRS, based on the testing done in the MIS program, which summarizes the LANL experimental work. The MIS testing shows that pure oxides contain an oxygen sink that essentially reduces the free oxygen to zero. The results indicate that while hydrogen is present in the cans, there is no flammable mixture because there is no oxygen present. The new DOE standard replacing the 3013 standard also states that oxides act as an oxygen sink. Two questions remain: will 9975 SARP certification reviewers accept the argument that there is no flammable mixture present and do impure oxides behave essentially the same as pure oxides. Impure oxides form a large percent of the oxide inventory.
PuF	There is an inventory of approximately 100 Kg of PuF. The PuF will be calcined and packed in produce cans and shipped to the SRS. There are approximately 600 cans of 330 g each (300 packages) if a higher limit is approved for the 9965, or 9975 shipping containers or approximately 2500 cans (2500 packages) if the 60 g (20 Ci) limit must be met. Gas generation is an issue. SRS is conducting tests on the PuF to quantify hydrogen and pressure generation. Testing has concluded that there will be a flammable mixture of gases. To date, the 9975 SARP authors intend to argue that the package can withstand pressures resulting from gas generation and/or that the flammable mixture is in the deflagration range and the resulting pressure and force will not breech containment. It is not clear that DOE certification reviewers will ultimately accept this approach.
SS&C	Sand, slag, and crucible (SS&C) is being packed at 330 g per can with the intent of shipping under the new 9975 SARP. After packing there may be as many as 2200 cans of SS&C which will need to be shipped to the SRS. Gas generation is an issue. The SRS is currently testing RFETS' SS&C material for pressure and gas generation. As for the PuF, results show that a flammable mixture may be generated. The approach for the 9975 CoC will be the same as for the PuF.
Samples	No package exists in which samples can be easily shipped from RFETS to SRS or LANL for testing. Shipments in the 9965 must show that they will not generate greater than 5% hydrogen during a one-year shipping period.

WIPP It is expected that the bulk of the contact-handled (CH) transuranic (TRU) waste will be shipped to the Waste Isolation Pilot Plant (WIPP) in the TRUPACT-II. There is approximately 3 MT Pu in 106 MT bulk not counting D&D generated waste. Some of the wastes have been tested in the Gas Generation Test Canister by J. B. Schierloh at RFETS for gas generation and are being packaged to meet WIPP requirements. A TRUCON code has been requested for solid inorganic material in metal cans with two to three weight percent water and an additional TRUCON code has been requested for incinerator ash – solid inorganics with up to 10% organic material. At this point it is unclear what the wattage requirements will be and how much material RFETS will be able to be put in a drum. The testing program for WIPP-bound material has repeatedly shown that the G values used to calculate hydrogen gas generation rates in the TRUPACT-II SARP are high by an order of magnitude. With the application of a 95% confidence level the TRUPACT-II wattage limits may be raised by a factor of three. The RFETS program has combined analysis and testing to meet the TRUPACT-II criteria, which reflect the NRC requirement of less than 5% hydrogen. Test program improvements have recently been identified that will increase efficiency and productivity. There is every indication that test program results will allow the NRC to increase the payload in the TRUPACT-II for the specific waste streams involved. It has been estimated that the testing program may result in a savings of approximately $12 million in repackaging and shipping costs. (Schierloh 1998)

Summary of Rocky Flats Shipping Needs

A certified package in which greater than 20 Ci quantities of Pu metal, oxides, and residue materials may be shipped. Resolution of the gas generation issues of impure oxides, PuF and SS&C for shipment in the 9975. Pure plutonium oxide and contact handled waste headed for WIPP have resolved hydrogen gas generation issues provided NRC certification reviewers accept the proposed resolutions.

3.2 SAVANNAH RIVER SITE (SRS)

The SRS Defense Waste Processing Facility will process nuclear material residues from RFETS, Hanford, LANL, and SRS. The Facility will stabilize the residues and prepare them for long term storage. The TRU wastes that are currently at SRS will be shipped to WIPP in accordance with the Federal Facility Compliance Act of 1992. In addition to the nuclear material residue processing and shipment of waste to WIPP, the SRS maintains the three certified packagings listed below.

The SRS is currently the holder of the following CoCs:

9965: The 9965 is a single containment package, therefore in accordance with 10 CFR 71.63 the user is limited to less than 20 Ci of plutonium per package. The CoC requires the user to demonstrate that there is less than 5% hydrogen by volume in a single confinement layer in a one-year shipping period.

9968: The 9968 is a double containment package with a small inner volume (1.1 L). The CoC requires the user to demonstrate that there is less than 5% hydrogen by volume in a single confinement layer in a one-year shipping period. The small inner volume makes the requirement difficult to meet.

9975: The current CoC allows the shipment of less than 20 Ci quantities of Pu metal, Pu Oxides, and SS&C and PuF residues with reduced moisture contents. The revised 9975 SARP that SRS is working on would raise allowable moisture levels and allow for greater than 20 Ci quantities of nuclear materials.

The SRS and LANL are conducting experiments to expand the payload of the SRS containers. The experimental work being conducted at SRS is directly applicable to the material at RFETS, Hanford, and LANL. Information on the PuF, SS&C, and oxide testing can be found in Section 3.1. Information on the LANL work can be found in Section 3.3.

3.3 LOS ALAMOS NATIONAL LABORATORY (LANL)

LANL has oxides, residues and metals similar in nature to RFETS. The materials will be shipped to the SRS in support of DOE's site weapons material deinventory policy. The TRU waste at LANL will be shipped to WIPP in accordance with LANL's Site Treatment Plan and agreements with the State of New Mexico. LANL currently has 9,000 m^3 of legacy TRU waste. Approximately 75% of the waste exceeds the wattage limits in the TRUPACT-II SARP and will have to be repackaged if the Payload Expansion Plan for the TRUPACT-II (see Section 3.5) is unsuccessful.

LANL is also the applicant for the SAFKEG 2863B package. Once certified, the SAFKEG 2863B will be used to ship a large variety of nuclear materials. The SARP for the package is still in the DOE certification review process.

The focus of the Materials Identification and Surveillance (MIS) Program at LANL has been to provide experimental support to expand the scope of the 3013 standard. It has also provided support to RFETS, SRS, and the Hanford Site through the testing of samples for hydrogen gas generation. In support of the 3013 standard the MIS project is tasked to 1) characterize representative materials and begin to characterize the 50% of the material in 3013 standard cans which is not plutonium, 2) show that materials can be brought into 3013 standard criteria conformance through thermal treatments and 3) demonstrate or develop methods to measure the parameters that are required by the standard. (Mason 1999)

To address these goals, material from Hanford, Rocky Flats, and Los Alamos have been examined. Nine canisters were received from Hanford and the examination of the storage containers and material they contain is complete. Material from twenty-four canisters containing plutonium from the Rocky Flats Facility are also complete. In addition, four items from the Los Alamos inventory were examined.

Examination of the materials have demonstrated that:

- Impure oxides were made to meet the 3013 standard LOI criterion by heating the material to 950°C for sufficient time. LOI, however, is only a moisture measurement method for pure materials and is not appropriate for impure plutonium containing materials.
- Moisture is a difficult measurement. It is a measure by a supercritical CO_2 fluid extraction method (SFE), an interstitial gas analysis method (IGA), and by a neutron moderation method (NM). The SFE and NM analytical methods were developed as part of the MIS project.
- LOI is not a measure of moisture but of the gases that are evolved at the measurement temperature. Evaporation or gas impurity volatilization, such as carbon, or copper oxides, or chlorides etc., and removal of reaction gases represent the bulk of weight loss in a LOI measurement.
- Stored actinide materials react with the oxygen and nitrogen in the can atmosphere and hydrogen and CO_2 gas are formed.

The surveillance part of the MIS effort continues. Nine surveillance reactors are loaded with materials provided by Hanford and Rocky Flats. Interim analysis has been performed on seven. In every case the pressure over these materials has dropped. In one item the pressure dropped significantly and most of that pressure loss was loss of oxygen.

Surveillance also includes monitoring Los Alamos 3013 standard cans equipped with bellows that are designed to monitor the pressure after long term storage. One can that began with a 2.1% LOI has slightly pressurized, a few psi, and all the pressure has not increased in any of the other cans.

The MIS effort also included an investigation of stress applied to storage containers when plutonium is cycled through temperatures that result in phase transformations. In addition to the characterization of plutonium bearing materials, the thermal performance of the materials in 3013 standard cans were investigated. (Mason 1999)

3.4 THE HANFORD SITE

The Plutonium Finishing Plant (PFP) at the Hanford Site has many of the same materials that are found on the Rocky Flats Site. The materials primarily consist of nuclear materials and plutonium processing residues. PFP, like Rocky Flats, is also driven by facility closure. In support of closure, all nuclear materials at PFP must be disposed of by the year 2005. The facility contains plutonium nitrates, plutonium and uranium mixtures with polystyrene, plutonium metals, plutonium fluoride, small quantities of other residues, and CH-TRU waste. Some of the materials will be processed and repackaged. Much of it will go to WIPP. At this point in time, the materials that represent the primary gas generation problem for transportation are the PuF cans. The PuF will be shipped to the SRS in the 9975 or the SAFKEG 2863B. The

SRS is currently testing PuF for shipment in the 9975. The results of the tests show that hydrogen gas is generated. As previously stated, the 9975 SARP demonstrates that the package maintains containment should a deflagration occur from the gas generated. The SARP is still in the review process and it is uncertain if the approach will be accepted by SARP certification reviewers.

In addition to the material at PFP, Hanford has a large quantity of low level TRU waste that will be repackaged and shipped to WIPP. Hanford's clean up efforts are governed in accordance with the site closure document (DOE 1998a). It is estimated that Hanford has a total inventory of 16,400 m^3 of TRU waste currently in storage with an additional estimated 9,250 m^3 of TRU waste that will be generated from D&D activities. The estimated drum equivalence of waste is 128,000 drums, of which 11,500 will come from PFP. Any TRUPACT-II payload expansion that allows higher decay heat limits and thus increases the payload allowed in a drum and reduces the number of drums and WIPP shipments will result in cost savings at the Hanford Site.

3.5 CARSLBAD AREA OFFICE

The Carlsbad Area Office in Carlsbad, New Mexico, manages the National Transuranic Waste Program and WIPP. The Office is responsible for managing WIPP and the safe disposal of TRU waste. As part of the effort to manage TRU waste the Carlsbad Area Office oversees the certification and transport of TRU waste. CH-TRU waste is discussed below.

CH-TRU waste will be packaged and sent to WIPP. The first WIPP shipment was made on March 26, 1999, paving the way for the many future shipments that will come from all sites in the DOE Complex. Each site has a large quantity of CH-TRU waste that will be or are packaged in 55-gallon drums, the standard waste box, or the ten-drum overpack. The containers will be packaged in the TRUPACT-II.

The TRUPACT-II SARP controls hydrogen gas generation through the implementation of decay heat limits. Each container is limited to a decay heat wattage based on the material types and confinement layers found in the container. All waste streams in the DOE Complex that will be disposed at WIPP will be assigned a TRUCON code that is cross referenced to a G value and a corresponding wattage limit depending on confinement layers. In some instances, for example Pu-238 wastes and solidified organic wastes, the decay heat wattage limits could drive sites to costly repackaging and a large increase in the numbers of drums. Therefore the TRUPACT-II Gas Generation Test Program and Payload Expansion Plan were initiated with the primary objective of establishing more realistic and less conservative G-values and expanding the payload of the TRUPACT-II. The Programs implemented payload expansion initiatives at various DOE sites.

The payload expansion plan for the TRUPACT-II contains many elements unrelated to gas generation testing. For details of the plan see *TRUPACT-II Payload Expansion Plan* (IT Corporation 1997). The elements of the plan that are associated with hydrogen gas generation include: a unified flammable gas test procedure, gas getters, and the matrix depletion program.

The unified flammable gas test procedure and the matrix depletion program are discussed below. Gas getters are discussed in Section 3.6.

3.5.1 Unified Flammable Gas Test Procedure

The unified flammable gas test procedure contains two initiatives: the evaluation and modeling of the flammability of mixtures of gases and volatile organic carbons (VOCs) and development of an alternative method to determine compliance with the limit on hydrogen gas concentration. The first of these initiatives has been completed and a mathematical model developed for determining the lower flammability limit of hydrogen gas with VOCs (Liekhus et al. 1998) (Loehr et al. 1998).

The second initiative is the development of a methodology for flammable gas testing that consolidates previous and existing test plans and expands the payload for test category (high decay heat or organic) wastes. The initiative includes research being conducted at Idaho National Engineering and Environmental Laboratory (INEEL) and at Rocky Flats. The INEEL drum testing used pre-existing test plans and experienced problems due to the instrumentation and setup. The testing program at INEEL is in a transitional period. The Rocky Flats testing (Schierloh 1998) has been highly successful. See the discussion in Section 3.1 under WIPP.

3.5.2 Matrix Depletion Program

The Matrix Depletion Program (MDP) experimental work was conducted at LANL. The experiments measured the dose dependency of G values on materials sprinkled with plutonium isotopes. Materials tested included wet and dry cellulose, polyethylene, PVC, and envirostone. The experimental work successfully showed that G values are dose dependent. The G values measured decreased as a function of dose and the resulting G values were in some cases an order of magnitude lower than the TRUPACT-II SARP G values. The work will be used to support a formal amendment to the NRC TRUPACT-II CoC for an increase in the payload of the package.

3.6 GAS GETTERS

Gas getters have the potential to mitigate hydrogen gas generation in packages containing a mixture of Class 7 and hydrogenous materials. Gas getters chemically scavenge hydrogen from the gas phase and bind it in a solid state. If gas getters can be shown to be reliable, they may expand the payload for packages containing nuclear materials, TRU waste intended for disposal at WIPP, and a wide variety of types of Class 7 materials.

To date, the NRC has not allowed gas getters to be used in NRC certified containers. The DOE Complex has used gas getters in Defense Programs applications, but EM-70 has not approved the use of gas getters in packages for hydrogen gas mitigation. The following questions have not all been successfully answered by any single gas getter currently available (courtesy of Phil Gregory, Westinghouse Electric, Carlsbad, New Mexico):

CAPACITY: What is the getter's capacity relative to the potential total gas generated during one year?
PRESSURE: What is the minimum normal operating pressure during one year? Is the getter's performance affected by pressure?
POISONS: Are there any chemical constituents in the contents that could potentially poison the getter?
REVERSIBILITY: Under what conditions will the getter release hydrogen and could these conditions occur during transport?
TEMPERATURE: What is the effective temperature range of the getter relative to the temperature conditions specified in 10CFR71 (-20F to 100F plus solar insolation)?
HUMIDITY: What is the effect of water vapor on the getter? Will a frozen getter still work?
LOCATION: Does the location of the getter matter? Consider stratification of the gasses.
THERMAL: Does the getter release/absorb heat? If so, is this factored into the thermal and structural analysis

Several attempts have been made to answer these questions. One of the TRUPACT-II Payload Expansion Plan initiatives was the Hydrogen Getters Project experimental work which was performed at LANL. The purpose of the project was to test the response of the hydrogen getter material, DEB, in the presence of gaseous compounds commonly found in the headspace of TRU waste drums. The intent of the project was to study the effect of the presence of gaseous compounds, such as VOCs, on the efficiency of the getter. (Mroz 1998) Of the functional groups and representative compounds that were tested it was found that chlorinated VOCs and carbon monoxide poisoned the getter material.   A path forward for the Hydrogen Getters Project is to develop a getter packaging that mitigates against the poisons in the form of a selective hydrogen permeable material. In addition, alternative catalyst formulations such as Pd-transition metal catalysts may reduce poisoning.

Another gas getter project is underway at the Hanford Site. Pacific Northwest National Laboratory (PNNL) has completed a year of engineering/fabrication development and performance testing for absorption kinetics and capacity of a new getter. The PNNL Composite Getter for hydrogen is an all-metal, coated two-piece zirconium-based getter capable of gettering hydrogen in air or inert atmosphere at ambient or elevated temperatures. The all-metal, coated zirconium-based getter has a metal coating providing a protective oxygen barrier while simultaneously allowing transport of hydrogen. The getter is shown to work in air at ambient temperature to 150-200°C or ambient to >300°C in inert atmosphere. The measured hydrogen gettering rate, based on present data to date, ranges from 25-50 cc STP/day/kg of getter directly in air. In inert atmosphere, such as in spent fuel casks, the rate is higher by 1000x. The hydrogen loading capacity of the getter is measured at 160 liters STP/kg of getter, regardless of atmosphere. The current tested configuration is a coated thin foil or coupon configuration. The Composite Getter is applicable for operation in air environments of normal oxygen concentrations and humidity, as well as inert gas, nitrogen atmosphere, or vacuum. With the coated two-piece getter design, it is currently expected that potential contaminating gases, such as halogenated VOC's, CO, or moisture, will not affect getter kinetics or capacity, since the atmosphere never comes in contact with the actual getter surface. Verification of this is currently planned in future testing. The PNNL Composite Getter is a promising new option for mitigation of hydrogen gas generation. It is estimated that an additional two years of research remains to be done before the getter may be used. (Baldwin et al. 1998)

4.0 SUMMARY AND CONCLUSIONS

Hydrogen gas generation issues are diverse and offer no simple generic solutions that may be applied across the board. Each of the DOE sites discussed in this report has materials that currently can not be shipped due to hydrogen gas generation issues. Materials of concern are roughly divided into nuclear materials (including oxides and residues) and wastes. DOE sites are on an accelerated schedule for cleanup in accordance with the Federal Facility Compliance Act of 1992, *Accelerating Cleanup: Paths to Closure* (DOE 1998b), and site-specific state agreements. As such, mitigation of the hydrogen gas generation issues is imperative to ensure timely compliance.

Research has been conducted at SRS and LANL to provide solutions for shipping pure plutonium oxides, fluorides, and sand, slag and crucible from RFETS to SRS. The 9975 SARP analysts are incorporating experimental data and research results into the 9975 which will be evaluated by certification reviewers in the near future. The SAFKEG 2863B SARP is also in the review cycle. The hydrogen gas generation and gas pressure issues in the shipment of impure oxides, a large part of the nuclear materials inventory, and assorted legacy materials have not been resolved.

The Carlsbad Area office is overseeing the shipment of waste to WIPP. Hydrogen gas generation issues in the transport of CH-TRU waste to WIPP are being addressed in the TRUPACT-II Payload Expansion Program. The Program has successfully adapted a multi-initiative approach. Testing at RFETS is expanding the allowable payload. The MDP has shown that G values are dose dependent and the research may result in an increase in decay heat limits per drum. Independent gas getter research at PNNL is promising and, if successful, could have applications for all types of hydrogen generating materials provided the PNNL gas getter also wins regulatory acceptance. Remote-handled-TRU waste and low-level waste hydrogen gas generation issues have not yet been raised or addressed.

Clarification of regulatory requirements is slowly coming. Still to be addressed are regulatory positions on getters, inerting to ensure that no flammable mixture is present, shipment of flammable mixtures provided containment can withstand a deflagration, or alternatively, an unequivocal position that a package must contain less than 5% hydrogen gas by volume. There is also some confusion about whether the volume of concern is defined as the inner confinement vessel or as any void space within a package. The NRC has tended to lean towards the need to unequivocally demonstrate that a package contains less than 5% hydrogen gas by volume in twice the expected shipping time. This philosophy, accepted by the TRUPACT-II applicants, has led to successful resolution of hydrogen gas generation issues in CH-TRU waste containers and it is expected that their efforts at payload expansion will have some success in the near future. As gas getter research shows new promise and MIS and SRS research characterizes the precise nature of gas components in nuclear materials, a combination of approaches may ultimately prove to be successful in the DOE community. However, a unified approach to solving the gas generation and pressure issues in nuclear materials packaging may be required for the successful resolution of regulatory concerns.

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